PHOSPHATE EQUILIBRIUM BETWEEN STREAM SEDIMENTS AND WATER: POTENTIAL EFFECT OF CHEMICAL AMENDMENTS

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ABSTRACT. *Sediments often play an important role in the temporary storage and release of phosphorus (P) in streams, especially streams receiving municipal wastewater treatment plant (WWTP) effluent. The objective of this study was to evaluate sediment−aqueous phase P equilibrium in four Ozark streams, and to determine the effect of alum ($Al_2(SO_4)_3$) and calcium carbonate ($CaCO_3$) on stream sediment−P interactions and content of exchangeable P. Stream physicochemical properties were significantly affected by the effluent discharge from the WWTPs; of particular interest to this study was that the increase in P concentrations varied greatly among streams. Phosphorus inputs from WWTP significantly increased sediment equilibrium P concentrations (sediment−EPC_0) and readily exchangeable sediment−bound P, while decreasing the P buffering capacity of stream sediments. Sediment−EPC_0 values were as great as 7 mg L^{-1} downstream from one WWTP, suggesting that sediments are a transient storage pool of P and may release P back into the stream system when P inputs from the WWTP are reduced. The addition of alum and $CaCO_3$ significantly reduced the sediment−EPC_0 and readily exchangeable P, while increasing the ability of sediments to buffer increasing P loads.*

Keywords. *Aluminum sulfate, Phosphorus, Sediments, Water quality, WWTP.*

Sediments often play an important role in the uptake, storage, and release of dissolved inorganic phosphorus (P) in aquatic systems (Meyer, 1979; Hill, 1982; Klotz, 1988), especially in streams receiving wastewater treatment plant (WWTP) effluent (Fox et al., 1989; House and Denison, 1998; Haggard et al., 2001). In general, stream sediments may act as a temporary P sink and possibly maintain aqueous−phase inorganic P concentrations at approximately the sediment equilibrium P concentration (sediment−EPC_0) (Taylor and Kunishi, 1971; Klotz, 1988). The effects of stream sediments on aqueous−phase inorganic P concentrations have been related to physical characteristics (Klotz, 1988; Baldwin, 1996); for example, sediment−EPC_0 is often correlated to the fraction of fine particles in sediments. However, several investigations have shown that biotic processes can affect the temporary retention or buffering of P by stream sediments (e.g., see Haggard et al., 1999).

Point sources of P from WWTPs impact sediment−EPC_0 and other sediment P properties in streams, and have been shown to be much greater than agricultural nonpoint sources of P in some catchments (Popova, 2000). The ability of stream sediments to buffer P concentrations was often decreased downstream of WWTPs, and sediment−P content was often significantly increased relative to sediment−P content upstream (House and Denison, 1998; Haggard et al., 2001). However, sediment adsorption is likely not the sole temporary sink of P in streams receiving WWTP effluent because it may not account for the total storage of P. For example, P may co−precipitate with calcium minerals in streams (House and Donaldson, 1986) and be immobilized from the water column by the microbial community (Gachter and Meyer, 1993) and macrophyte beds (Chambers and Prepas, 1994). Thus, the fate of P in streams receiving WWTP effluents depends greatly on interactions with sediments and the associated biota.

Sediments are often long−term sources of P to aquatic systems (especially lakes and reservoirs) after external P inputs from the watershed have been reduced or removed (Larson et al., 1979; Ryding, 1981). The flux of P from bottom sediments is often much greater under anaerobic conditions in the hypolimnion of lakes and reservoirs than under aerobic conditions (James et al., 1995). Chemical amendments, e.g., aluminum sulfate [alum ($Al_2(SO_4)_3$)], can be used to bind readily exchangeable P in sediments and P adsorbed to minerals subject to reduction when overlying waters are anoxic (Kennedy and Cooke, 1982; Welch and Schrieve, 1994). The use of alum may be a viable option to treat and reduce elevated levels of readily exchangeable sediment P in impacted streams, such as downstream from WWTPs. Alum has successfully reduced P concentrations and loads in WWTP effluent and urban stormwater runoff (Harper et al., 1998).

The focus of the present study is the Illinois River and Flint Creek Basin in the southwestern portion of the Ozark Plateaus in northwest Arkansas and northeast Oklahoma. In

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the southwestern Ozark Plateaus, municipal WWTPs have been identified as a major contributor to stream P concentrations and export in regional catchments. Average annual P export from the Illinois River Basin was approximately 208,000 kg year^{-1} near the Arkansas and Oklahoma state boundary from 1997 to 2000 (Haggard et al., 2003). Contributions of P from the WWTPs were estimated to be approximately 93,000 kg year^{-1} to the Illinois River (White et al., 2002), or almost 45% of the average annual stream P load. The objective of this study was to evaluate P equilibrium between stream sediments and water upstream and downstream of four municipal WWTPs. We also evaluated the use of a chemical amendment *in vitro* to reduce sediment P release and availability into the overlying water.

METHODS

Water and sediment samples were collected in four headwater streams, all of which receive effluent from municipal WWTPs. Water−quality samples were collected from midstream during base−flow conditions at sites upstream of municipal WWTPs (serving as background or reference conditions) and at four sites downstream at Mud Creek, Osage Creek, Spring Creek, and Sager/Flint Creek in July 2002. These creeks receive WWTP effluent from the cities of Fayetteville, Rogers, Springdale, and Siloam Springs, Arkansas, respectively. Water samples were collected using HDPE syringes, filtered through a 0.45 μm nylon membrane, acidified to pH <2 using HCl, and either stored on ice or refrigerated (4°C) until processing. Water samples were analyzed for soluble reactive P (SRP) concentrations using the ascorbic acid reduction method (APHA, 1992).

Composite sediment samples were collected along transects perpendicular to streamflow at sites upstream of municipal WWTPs and at three sites downstream at each stream; a single composite sediment sample was collected from at least five sites along a transect at each site. Stream sediments were collected from the top 2 to 5 cm of the benthic zone using a trowel, placed into plastic bags, and kept on ice or refrigerated in the dark until processing. Sediment samples were sieved through 4.5 mm sieve, and particles <4.5 mm were used to determine exchangeable P (sediment−ExP) and sediment−EPC_0. The amount of readily exchangeable P loosely sorbed to sediments (sediment−ExP) was extracted from wet sediments using 100 mL of 1 M $MgCl_2$ in an Erlenmeyer flask (Ruttenburg, 1992). A known amount (20 to 30 g) of fresh, wet sediments was shaken with the $MgCl_2$ solution at low speed for 1 h, and then a 15 mL aliquot was filtered through a 0.45 μm nylon membrane. The remaining sediment slurry was transferred to a preweighed aluminum pan and oven−dried at 80°C for 48 h for dry weight determination. Sediment−ExP in this study represented an extremely conservative estimate of exchangeable P, as we extracted only the most loosely sorbed P with this single extraction.

Sediment−EPC_0 is defined as the aqueous−phase P concentration at which net P adsorption and desorption by unaltered stream sediments is zero (Taylor and Kunishi, 1971). We used filtered stream water spiked with additional soluble P at rates of 0, 0.10, 0.25, 0.50, and 2.00 mg L^{-1}; for example, if the filtered stream water had an ambient SRP concentration of 0.10 mg L^{-1}, then the series of P standard solutions in filtered stream water initially contained 0.10, 0.20, 0.35, 0.60, and 2.10 mg SRP L^{-1}. We added 100 mL of the various P standard solutions from filtered stream water to 20 to 30 g wet sediments, and the sediment slurry was shaken, filtered, and dried as previously described. The amount of P sorbed per dry weight sediment (mg P kg^{-1} dry sediment) was regressed against initial P concentration of the standard solutions (mg L^{-1}), and EPC_0 was estimated as the *x*−intercept of this plot (fig. 1). The slope (K) of this linear relation may be interpreted as a measure of the ability of sediments to adsorb, or buffer, increases in ambient P concentrations of the aqueous phase, with greater K values suggesting an increase in the amount of P sorbed (mg P kg^{-1} dry sediment) per unit increase in aqueous P concentration (mg L^{-1}).

Approximately, 250 g wet sediments from each site were mixed with 0.5 g aluminum sulfate (alum, $Al_2(SO_4)_3$) and 0.5 g calcium carbonate ($CaCO_3$) for 5 min; $CaCO_3$ was used

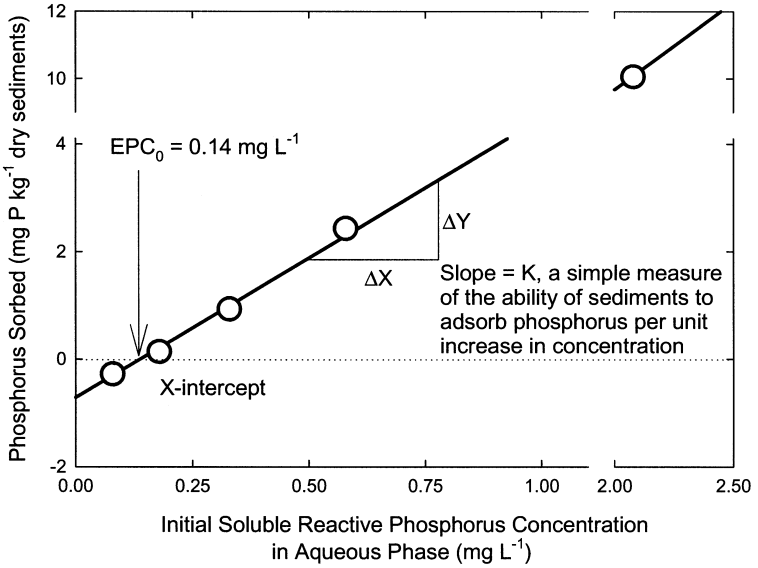

Figure 1. Example of sediment−EPC_0 estimation using the simple linear regression of P sorbed by sediments as a function of initial SRP concentration in the aqueous phase during extractions from an Osage Creek site 1.5 km downstream from WWTP in July 2002.

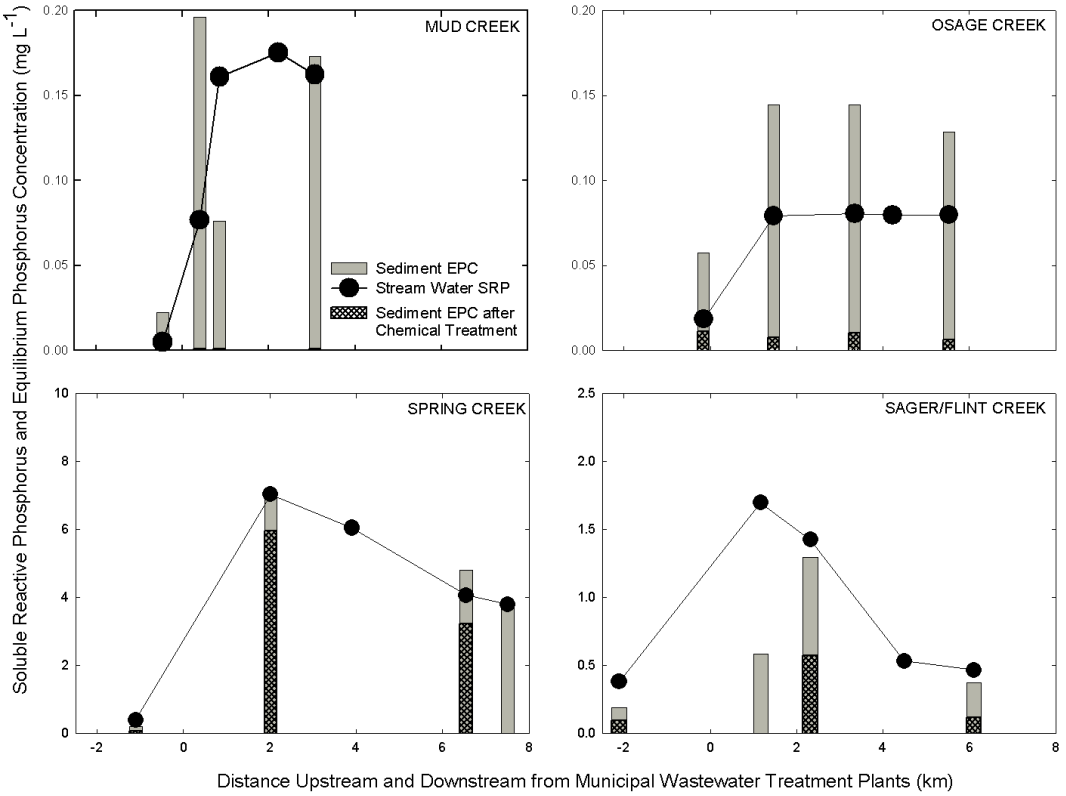

Figure 2. Soluble reactive phosphorus in the water column and sediment−EPC_0 with distance upstream (negative) and downstream from municipal wastewater treatment plants at Mud, Osage, Spring, and Sager/Flint Creeks in July 2002.

to buffer pH because we wanted to mitigate the acidifying effect of alum. Sediment slurry pH was measured before (7.6 ±0.3) and after (6.6 ±0.2) chemical amendments were added and well mixed. Sediment extractions as previously described were conducted on all "treated" sediments from each sampling site.

Statistical analyses are described for each specific comparison, and an *a priori* significance level of $\alpha = 0.10$ was selected.

RESULTS

The effect of municipal WWTP effluent on SRP concentrations in the water column differed among streams (fig. 2). Soluble P in Spring Creek at the first site downstream from the WWTP increased 17× compared to that upstream, whereas in Mud, Osage, and Sager/Flint Creeks soluble P increased approximately 4×. However, the effect on water column concentrations was least in Mud and Osage Creeks,

Table 1. Simple linear regression of P sorbed by sediments as a function of initial SRP concentration in the aqueous phase during sediment−EPC_0 extractions before and after chemical treatment, where K (slope) denotes a simple measure of sediment P buffering capacity, and EPC_0 is defined as the *x*−intercept of this linear relation.

		Before Treatment				After Treatment			
July 2002 Stream	Distance (km)	K (slope)	EPC_0 (mg L^{-1})	r^2	p	K (slope)	EPC_0 (mg L^{-1})	r^2	p
Mud	−0.5	6.08	<0.01	0.99	<0.01	7.20	0.03	0.99	<0.01
	0.4	4.07	0.18	0.99	<0.01	5.79	<0.01	0.99	<0.01
	0.9	5.71	0.06	0.99	<0.01	5.92	<0.01	0.99	<0.01
	3.1	3.72	0.09	0.99	<0.01	6.13	<0.01	0.99	<0.01
Osage	−0.2	5.85	0.02	0.99	<0.01	6.04	<0.01	0.99	<0.01
	1.5	5.13	0.14	0.99	<0.01	5.67	<0.01	0.99	<0.01
	3.4	5.37	0.12	0.99	<0.01	4.84	<0.01	0.99	<0.01
	5.5	5.03	0.14	0.99	<0.01	4.67	<0.01	0.99	<0.01
Spring	−1.1	6.35	0.13	0.99	<0.01	5.79	0.07	0.99	<0.01
	2.0	5.19	6.99	0.97	<0.01	5.58	3.98	0.84	0.03
	3.9	4.70	5.21	0.97	0.01	5.82	1.31	0.81	0.04
	7.5	6.13	3.68	0.99	<0.01	6.14	<0.01	0.96	<0.01
Sager/Flint	−2.1	5.20	0.12	0.99	<0.01	5.67	0.08	0.99	<0.01
	1.2	4.94	1.05	0.99	<0.01	6.11	0.13	0.99	<0.01
	2.3	5.04	1.27	0.99	<0.01	6.53	0.32	0.99	<0.01
	6.1	5.22	0.32	0.99	<0.01	6.15	0.10	0.99	<0.01

greater in Sager/Flint Creek, and greatest in Spring Creek. SRP concentrations generally decreased downstream from point sources of P, as observed in Spring and Sager/Flint Creeks, but SRP concentrations in Mud and Osage Creek were relatively stable with increasing distance downstream from the WWTPs.

Similar to water column SRP concentrations, sediment−EPC_0 significantly increased (paired t−test for ln transformed data, $p < 0.05$) at all streams below the WWTPs (table 1, fig. 2), and the increase in sediment−EPC_0 was generally proportional to the increase in water column SRP across all streams. A strong relation existed between sediment−EPC_0 and water column SRP across all streams ($\ln EPC_0 = 1.27 \ln SRP - 1.75$, $r^2 = 0.85$, $p < 0.001$); however, data from individual streams suggested that sediments were a source, a sink, or in equilibrium with the aqueous phase. Sediment−EPC_0 significantly decreased (paired t−test for ln transformed data, $p < 0.001$) at all sites when benthic sediments were treated with alum and $CaCO_3$ (table 1, fig. 2), although the decrease was relative to the level of P enrichment from the WWTP.

We observed a significant positive relation (simple linear regression for ln transformed data, $r^2 = 0.90$, $p < 0.001$) between ExP and EPC_0 across these streams. Exchangeable P (ExP) in this study represents a very conservative estimate of the loosely or readily exchangeable P and is intended for relative comparisons among sites, streams, and treatments (fig. 3). It was obvious that WWTP effluents significantly increased the pool of sediment−bound P at these streams (paired t−test for ln transformed data, $p < 0.01$), and ExP did not sequentially decrease with increasing distance downstream from WWTP effluent discharge. Sediment−ExP significantly decreased (paired t−test on ln transformed data, $p < 0.001$) at sites downstream from the WWTPs when benthic sediments were treated with alum and $CaCO_3$ (fig. 3).

The slope (K) of the relation between P sorbed and initial SRP concentrations was also significantly greater (paired t−test on ln transformed data, $p = 0.08$) at sites upstream (average K = 5.87) from the WWTPs compared to that immediately downstream (average K = 4.83) (table 1). The slope (K) of the relation between P sorbed and initial SRP concentrations was also significantly greater after sediments were treated with chemical amendments (paired t−test on ln transformed data, $p = 0.01$), further suggesting an increase in the ability of sediments to adsorb P from aqueous solutions.

DISCUSSION

Phosphorus concentrations in streams generally show a sequential decrease with increasing distance from municipal WWTP effluent discharge (e.g., see Fox et al., 1989; Chambers and Prepas, 1994; House and Denison, 1998; Haggard et al., 2001, 2004). Streams often require kilometer−scale distances to temporarily retain significant portions of P inputs from WWTPs (Haggard et al., 2001, 2004; Martí et al., 2004). In Spring Creek and Sager/Flint Creek, the sequential decrease in SRP concentration was likely from sediment sorption, biotic uptake, and dilution from groundwater and lateral tributaries.

Benthic sediments often play an important role in the temporary retention and release of P in stream systems. The inputs of P from WWTPs increased the sediment pool of readily bioavailable P at these streams, and reduced the P

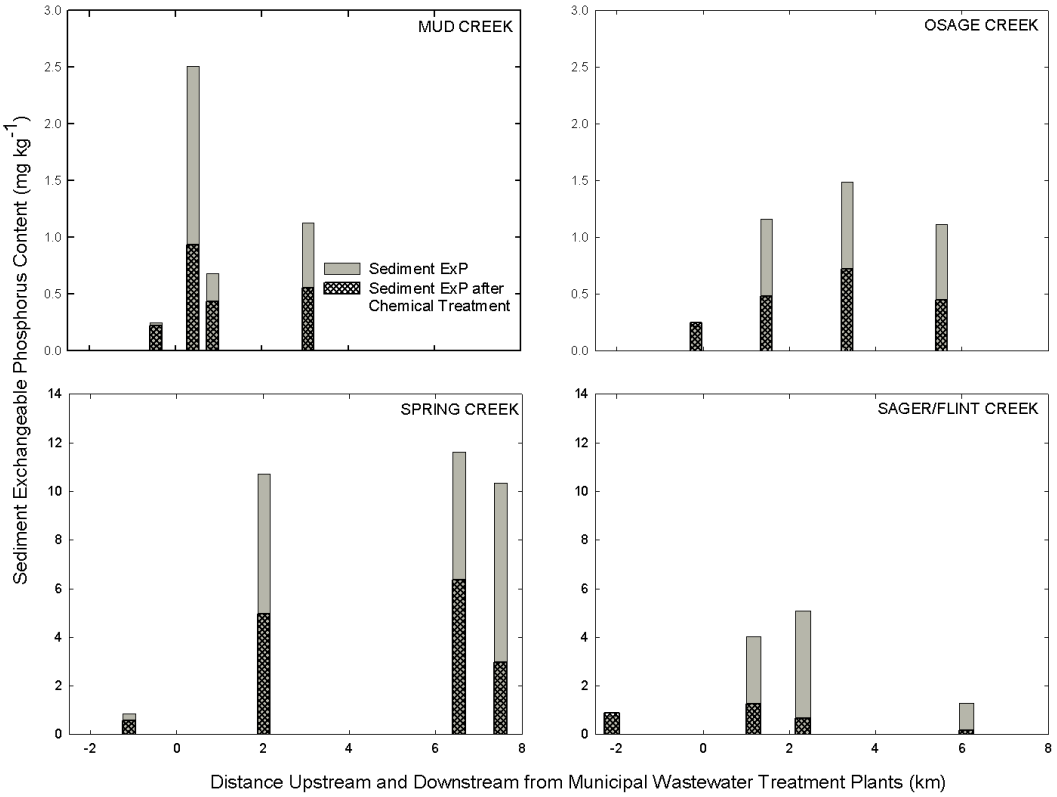

Figure 3. Sediment−ExP with distance upstream (negative) and downstream from municipal wastewater treatment plants at Mud, Osage, Spring, and Sager/Flint Creeks in July 2002.

buffering capacity. Several studies have shown similar results, suggesting that abiotic processes (sediment sorption) are a substantial factor in P retention (Fox et al., 1989; House and Warwick, 1999) but are not solely responsible for decreases in P concentrations downstream from WWTPs; biotic processes were also important determinants (Chambers and Prepas, 1994; House and Denison, 1998). However, it is possible for enriched systems to become saturated with P and even release P when inputs are reduced below a threshold concentration (Haggard et al., 2004). The amount of loosely exchangeable P in benthic sediments was strongly correlated to EPC_0, as has been observed in streams with finer sediments in the south−central Great Plains of Oklahoma (Haggard et al., 1999). Sediment−EPC_0 appears to be influenced by the amount and availability of P in sediments, which is directly influenced by external P additions from the watershed, especially WWTPs.

Sediments represent a transient storage pool of P in stream systems, especially those receiving WWTP effluent with high amounts of P. It is conceivable that once effluent P concentrations are reduced at Spring and Sager/Flint Creeks to the newly adopted 1 mg P L^{-1} effluent limit, benthic sediments will release P into the water column and maintain elevated P concentrations for several kilometers downstream for an undetermined period of time. Bottom sediments are often sources of P in aquatic systems, especially lakes and reservoirs (James et al., 1995), and chemical remediation may be used to reduce sediment P flux (e.g., James et al., 2000; Burley et al., 2001). Alum additions have been suggested as an effective remedial action to inactivate loosely exchangeable and iron−bound P in lake and reservoir sediments (Rydin and Welch, 1999). The effect of alum and $CaCO_3$ on benthic sediment adsorption, or buffering, of aqueous−phase P in these streams was very similar because chemical treatment reduced ExP and increased P buffering capacity (K). Sediment−EPC_0 was subsequently decreased after chemical treatment, and therefore would reduce the P concentrations where sediments and the aqueous phase are in equilibrium. These streams (Spring and Sager/Flint Creeks) will eventually recover from elevated P inputs and likely have similar SRP concentrations to Mud and Osage Creeks, where the WWTPs already operate with a 1 mg L^{-1} limit on effluent P concentrations.

Alum treatment to reduce P availability or loss has been used in soils (Gilbert et al., 2003) and urban stormwater runoff (Harper et al., 1998), as well as lakes and reservoirs (see previous citations). Thus, alum treatment of streams may be a feasible option to mitigate P release from benthic sediments after external P sources are reduced. The use of alum in streams to reduce sediment−EPC_0 and P availability requires further research on the effects of alum floc on stream habitat and biota. This study showed the potential benefit of alum treatment to stream sediments *in vitro*, and the next step should be larger−scale studies in stream reaches or artificial stream mesocosms.

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